

TITLE: Mass Balance Assessment of Pesticides and Nutrients
Applied to Golf Turf - Volatilization and Dislodgeable
Residues

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USGA REGION: Northeastern/Mid-Atlantic

EXECUTIVE SUMMARY

Title: Mass Balance Assessment of Pesticides and Nutrients Applied to Golf Turf-Volatilization and Dislodgeable Residues.

Location: Massachusetts Pesticide Analysis Laboratory (MPAL), University of Massachusetts-Amherst.

Progress and Results. (1/15/91 to 11/1/91): In the past 9 months, this laboratory has been responsible for the hiring, training (both academic and technical) and quality control for a full-time Ph.D. graduate student (Casey Murphy), a 1/2-time residue chemist (M.W. Brooks) and a 3/4-time work study technician (B. Chase). Relevant literature was reviewed concerning the environmental monitoring of mecoprop, triadimefon and trichlorfon. Procedures for the analysis of these three pesticides, both as airborne volatile and dislodgeable residues, were evaluated, modified, developed and implemented. Detection levels, extraction efficiencies, linearity of standard curves, interference due to environmental contaminants, mass balance recoveries from sampling devices and storage ability have been determined.

Upon method verification for triadimefon and trichlorfon, these materials were applied to turf (8/23/91-triadimefon and 9/28/91-trichlorfon). Volatile and dislodgeable samples were collected over a two week sampling period. Samples were extracted and prepared for storage. Quantitation of these samples is now under way at MPAL.

Evaluation of new derivatization methods to analyze mecoprop is currently being carried out and method verification for the analysis of isazofos will be initiated in 1992. Once concluded, these two pesticides will be applied to our experimental turf plot during the 1992 growing season.

Percentage of time devoted to the research program by UMASS/MPAL personnel. Murphy-100%, M.W. Brooks-50%, B. Chase-50%, A.S. Curtis-10%, D. Tessier-5%, J.M. Clark-5%, R.J. Cooper-5%.

Itemization of expenditures made during the year (as of 10/5/91). Personnel (\$3726.27), Supplies and replaceable equipment (\$6248.64), Overhead (\$669.63), Total to Date (\$10,674.54).

PROGRESS AND RESULTS

I. ANALYTICAL AND LABORATORY TECHNIQUES

A. Academics and Related Work Experience (Casey Murphy, Ph.D. Candidate, Dept. of Chemistry)

Academic courses taken at the graduate level before fall of 1991 and presently enrolled in (*):

Advanced Inorganic Chemistry	Chemistry of the Elements
Advanced Organic Chemistry	Spectroscopic Methods of Chemistry
Theoretical Chemical Analysis	Coordination Chemistry
Physical Methods of Chemistry	Statistical Chemical Analysis*

During the summer of 1990, Ms. Murphy worked full-time as an analyst in the Water Resources Research Center, UMass, Amherst. She was responsible for sample preparation and quality control/quality assurance (QC/QA) aspects in the quantitation of nitrate and phosphate content of water samples.

From January 15 through November 1 of 1991, 100% of her time effort has been devoted to this project (USGA/MPAL). A XAD-4 resin from Rohm and Haas was selected for the collection of volatile pesticide residues from air and Fischer's analytical-grade cheesecloth was selected to collect dislodgeable pesticide residues from turf. Method development for pesticide analysis from these two environmental matrices has been pursued. During this initial period, many aspects of pesticide analytical chemistry and chromatography have been acquired.

B. Instrumentation

1. High Pressure Liquid Chromatography (HPLC). A HPLC system with an ultraviolet (UV) detector had been utilized for mecoprop (MCP) analysis^{1,2}. Co-eluting contamination peaks forced a variety of silica analytical columns

(e.g., octadecyl and cyanopropyl) and mobile phases (e.g., acetone/nitrile/water and methanol/water) to be examined. These variations were explored under both normal and reverse-phase chromatography conditions.

2. Gas Chromatography (GC). The remaining three compounds (i.e., triadimefon, trichlorfon and isazofos) can be analyzed by GC^{3,4,5}. Two GC systems utilizing three different detectors: flame photometric detection (FPD), nitrogen-phosphorus detection (NPD), and electron-capture detection (ECD) have been formatted to accomplish these analyses.

C. Sample Preparation Techniques

1. Solid Phase Extraction (SPE). Working with environmental samples from two different matrices requires extensive sample preparation before any quantitative determination of pesticide residues can take place. Methods of SPE to remove interfering environmental contamination have been determined as a cleanup step in both apolar and ionic phases of SPE^{2,3}. To reach acceptable detection limits, samples must be concentrated without the loss of any compound. Two such methods have been utilized in this study (see Results section III).

2. Derivatization. The various methods of derivatization to make a compound thermally stable and volatile for GC analysis have been reviewed^{6,7,8}. One method has been selected for MCPP analysis and should eliminate the co-eluting contaminants that have been a problem in the previously described HPLC method⁸. Also, detection limits should be greatly improved.

D. Sample Analysis

Once the sample is prepared and injected into an instrument, the pesticide of interest must then be correctly identified and quantitatively assessed. The concepts of standard curves, daily spikes, daily blanks, storage spikes, replicate treatments, internal and external standards have been studied and incorporated into routine sample analysis.

Spectra-Physics integration and data acquisition software is available on IBM computers at MPAL. The proper operation of this system allows the data on chromatograms to be more accurately evaluated and easily stored for future publication. Word Perfect and Chemtext are word processing programs that allow rapid text production and data reduction processes.

II. *FIELD SAMPLING TECHNIQUES*

A. Experimental Theory

1. Measurement of Volatile Pesticide Residues in Air. The rate of volatile pesticide loss from the treated turf is measured with J.D. Wilson's Trajectory Simulation Method (TSM).⁹ A high volume air sampler is suspended at a predetermined height (ZINST) in the center of a circular plot. As air is pulled through the collector (at approximately 26 cubic feet per minute (CFM)), the pesticide vapors recondense onto a XAD-4 resin trap. Extraction of the pesticide from the trap resin with an organic solvent (e.g., acetone or methanol) will give the concentration of the pesticide at that one height. The actual ZINST is determined using a meteorological modeling system and is dependent upon the radius of the plot and the roughness height of the turf. Dr. Wilson has determined ZINST to be 70 cm for our plots (10 m radius) at a roughness height of 0.2 cm.

2. Measurement of Dislodgeable Pesticide Residues. The dislodgeable residue method used in the past by our laboratory was reviewed¹⁰, and an alternative method which is more representative of human exposure on a golf course was chosen¹¹. A one square foot area of pesticide-treated turf is wiped with a piece of water-dampened, pre-extracted, cheesecloth. Similar to the resin, extraction of the cheesecloth with an organic solvent, followed by a cleanup and concentrating step, will give the quantity of the dislodgeable residues available at that time.

B. Preparation/Maintenance of Experimental Turf Plots

1. Initializing and Maintaining Turf. The University of Massachusetts Turf Farm is located in South Deerfield, MA. In May of 1991, approximately 0.5 acres of turf was desodded, tilled, raked and prepared for seeding. On June 17, 1991, the plot was seeded with Penncross creeping bentgrass. Throughout the summer, the turf was clipped at a height of 1/2 inch. Maintenance simulated that of a golf course fairway: mowing three times a week with watering and pesticide applications (i.e., pesticides of non-interest to study) applied as needed.

2. Application of Pesticides of Interest. On the morning of August 23, 1991, the systemic fungicide, triadimefon (trade name, Bayleton), was applied to a 10 m radius plot. A fifteen foot, twelve nozzle, spray boom applied the water formulation at a rate of 2 oz/3 gal/1000 ft². Volatilization and dislodgeable residues sampling started at the time of application and continued for a two week period according to the sampling schedule (see Section II. D).

Approximately one month later, on the morning of September 28, 1991, the non-systemic insecticide, trichlorfon (trade name, Proxol 80 SP), was applied at a rate of $2\frac{3}{4}$ oz/3 gal/1000 ft². The same spray boom was used and a 10 m radius plot was sprayed. Sampling followed for the next two weeks as scheduled (see Section II. D).

C. Meteorological Data Capture

A Campbell CR10 Weather Station was set up in the southwest corner of the plot, which is normally downwind of the high volume air sampler. Wind speed, wind direction, surface and air temperature, solar radiation and rainfall are sensed every minute and a sixty minute average of the data is collected in a storage module. After the two week sampling period, this storage module was disconnected, brought back to the laboratory and the weather data transferred to an IBM computer for permanent storage and analysis.

D. Sampling Schedule

VOLATILES

<u>Day 1</u>	<u>Day 2</u>	<u>Day 3</u>
7 - 9 a.m. (pre-sample)	7 - 11 a.m.	7 - 11 a.m.
9 - 11 a.m. (during spray)	11 a.m. - 3 p.m.	11 a.m. - 3 p.m.
11 a.m. - 3 p.m.	3 - 7 p.m.	3 - 7 p.m.
3 - 7 p.m.	7 p.m. - 7 a.m.	
7 p.m. - 7 a.m. (overnight sample)		

Days 5, 7, 10 and 15

9 a.m. - 1 p.m.
1 p.m. - 5 p.m.

00105

DISLUDGEABLES

Day 1

8 a.m. (pre-sample)
9:20 a.m. (15 min post-application)
5 p.m. (8 hrs post-application)

Days 2, 3, 5, 7, 10 and 15

all samples taken at 12 noon

III. RESULTS

A. Method Development

1. Mecoprop ((MCPP).

a. Extracting and Concentrating Samples. 100 ml of XAD-4 resin amended with MCPP (10 and 50 ppm) was extracted with 150 ml of acetone. The flask containing the resin/acetone mixture was agitated on a wrist-action shaker for one hour. The slurry of resin and acetone was filtered through Whatman #1 filter paper and the eluant collected into a 500 ml round bottom flask. The resin was rinsed with 2 x 50 ml of acetone and the eluants pooled.

Cheesecloth was amended with MCPP in a similar manner. 150 ml of acetone added to a flask containing the treated cheesecloth and this was shaken for 15 min. The solvent was decanted through filter paper into a 500 ml round-bottom flask. An additional 100 ml of acetone was added and the flask shaken again for 15 min. This was also poured into the round bottom flask through the filter paper. The cheesecloth was washed with 2 x 20 ml of acetone and this solvent was collected in the round-bottom flask. Samples were concentrated by vacuum to 10 ml. 100 ml of deionized-distilled water (ddw) was added and the pH adjusted to less than 3 with the addition of hydrochloric acid (HCl)

b. Sample Cleanup with SPE². A 500 mg, 6 ml octadecyl C₁₈ SPE cartridge was prepared with 2 x 6 ml washes of methanol (MeOH) and 2 x 6 ml

washes of water (pH= 2.65 with HCl). Then 110 ml of a 10% acetone/water sample solution was passed through the C₁₈ column at a rate of 5 ml/min. Excess water was removed by vacuum and the compound eluted off of the SPE column in 5 ml of the MeOH.

c. HPLC Analysis. A HPLC system with an u-Bondapak C₁₈ (3.9 x 300mm) analytical column, a UV detector set at 233 nm, a mobile phase of 50% acetonitrile/water (pH of water is 2.68 with acetic acid) at a flow rate of 1 ml/min was utilized to analyze MCPP. Although extensive sample preparation was included, this method resulted in co-eluting contamination peaks which interfered with analysis.

d. Variations of the Method to Remove the Interfering Peaks. Various methods of sample cleanup were attempted to remove the interference. An anion exchange SPE column and a C₁₈ SPE column under basic conditions followed by a C₁₈ column under acidic conditions were both tried. This did not isolate the MCPP from contaminants so these variations were tried with different analytical SPE columns (e.g., a cyanopropyl column under reverse phase chromatographic conditions and a silica column under normal phase chromatographic conditions). Next 1% tetrabutyl ammonium phosphate was added to a nonacidified mobile phase used in the HPLC analysis. An ion pair is formed between the MCPP and the tetrabutylammonium which will then give longer retention times for the compound. Nevertheless, all of the above efforts to remove the co-eluting interferences did not resolve MCPP to allow analysis.

e. Methods of Derivatization. In the literature there are various methods to derivatize MCPP to make it thermally stable and volatile for GC analysis^{6,7,8}. One such method has been selected and will be used in determining MCPP⁸. This method offers reproducibility and selectivity, and should eliminate the interfering peaks seen in the HPLC method.

2. Triadimefon.

a. Extracting and Concentrating the Samples. The extraction method for triadimefon from XAD-4 resin and cheesecloth is exactly the same as for that used for MCP. The extraction solvent was reduced to a volume of 10ml and then diluted with 100 ml of dd water.

b. Cleanup with SPE². A C₁₈ SPE cartridge described above was used in triadimefon sample cleanup. It was prepared by washing with 2 x 6 ml 10% methylene chloride solution in methanol (MeCl₂/MeOH), 2 x 6 ml MeOH and 2 x 6 ml 10% acetone/water solutions. The analytical sample was passed through the column and 5 ml aliquot of hexane was used to wash the column. A 5 ml aliquot of 10% ethyl acetate/iso-octane solution eluted triadimefon from the SPE column.

c. GC Analysis². A Hewlett Packard 5890 GC system with a DB-17 (15 m x 0.245 mm) column and a NP detector (NPD) was used for the analysis of trichlorfon. The injector temperature was 250°C and the detector 300°C. The initial column temperature at 140°C for 2 min which was increased 8°C per min to a final column temperature of 200°C for 2 min. The 5/1 signal to noise detection limit was 0.05 ug/ml (50 ppb) and the extraction efficiencies were 85% from the XAD-4 resin and 100% from the cheesecloth.

3. Trichlorfon.

a. Extraction and Concentrating of Samples. The solvent extraction of resin and cheesecloth follows the same protocol as for MCP and triadimefon, except that all of the resin must have an acid water wash (pH < 4 with HCl). The resin is then rinsed and dried prior to trichlorfon treatment. This is necessary to prevent any of the trichlorfon from immediately breaking down to dichlorvos under natural and basic conditions on unacidified resin. The sample is reduced to 5 ml under vacuum and quantitatively transferred to a 13

ml graduated centrifuge tube by two washes of 2 ml acetone which is then pooled in a centrifuge tube. The acetone extract is condensed under N₂ to 0.5 ml and MeCl₂ is added to a total volume of 5 ml. The sample at this point is ready for injection.

b. GC Analysis⁴. The model 5890 Hewlett Packard GC with a DB-1 (30 m x 0.541 mm) column and FP detector (FPD) is used for trichlorfon quantification. The following instrument settings were used: injector port 130°C, detector 300°C, initial column temperature 120°C for 1 min, then increased by 15°C per min to a final column temperature of 150° for 8 min. The 5/1 signal to noise detection limit was 0.08 ug/ml (80 ppb) and extraction efficiencies from the resin was 87% and 100% from the cheesecloth.

B. Sample Analysis

1. Triadimefon.

a. Volatiles. At the end of a sampling period, the resin from the high-volume air sampler was quantitatively transferred into a 250 ml amber glass storage bottle. Excess resin was rinsed with acetone into the jar. The amber bottle was capped and refrigerated immediately at the Turf Farm until transported that evening back to MPAL where they were then stored in a freezer at -20°C. Within one week, the samples were extracted as described in the method section and the solvent returned to the freezer until further analysis. With each batch of extractions, a daily spike was made on pre-cleaned resin which served as a percent recovery indicator of triadimefon for that day.

b. Dislodgeables. At noon of each scheduled sampling day, dislodgeable residue samples were taken. A square foot wooden frame was placed on the turf. A 9" x 3 1/2" water-dampened piece of cheesecloth was vigorously wiped across the grass right to left in five strokes. Opening the cloth and folding

so the other side was exposed, the turf was then wiped left to right. Any grass blades that adhered to the cloth were lightly shaken off. The cheesecloth was immediately put into a 250 ml amber glass storage bottle. This procedure was repeated three more times on separate turf areas. All four wipe samples were pooled and comprised one dislodgeable sample for that day. The sample was immediately capped and refrigerated until transferred to a MPAL freezer that evening.

c. Storage Spikes. Each evening of a sampling day, 10 ug of a triadimefon standard solution was administered (i.e., spiked) to clean resin and to cheesecloth. These were stored in the freezer with the collected samples and served in assessing storage losses, if any.

2. Trichlorfon.

Knowing how unstable trichlorfon is on resin beads⁴ or any other absorbent, it was decided to extract the volatile samples and the dislodgeable samples as soon as possible after collection.

a. Volatiles. Immediately after a sampling period, the resin beads were transferred to a flask and extracted as described in the method section. The solvent was stored in the refrigerator at the Turf Farm until transferred to a freezer that evening at MPAL.

b. Dislodgeables. The sampling technique is the same as that as described for triadimefon dislodgeables. Extraction of the cheesecloth follows the same method as described in the methods section. The solvent was stored in the refrigerator at the Turf Farm until transferred to a freezer at MPAL.

c. Daily and Storage Spikes. Each day samples were extracted, 50 ug of a trichlorfon standard solution was administered (i.e., spiked) to both resin and cheesecloth and extracted at the same time as the collected samples.

These daily spikes will serve to quantitate the extraction efficiencies for that day. In addition, a 50 ug spike of trichlorfon was added to 100 ml of acetone and stored in the freezer with each batch of collected samples. This serves as a storage spike to determine any losses, if any, incurred during storage.

00111

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